I

Claims

1. Compound of the general formula I

 $R^{11} - A_a - Z^{11} - O_b - D_d - Y^{11}$

in which

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R¹¹ denotes H, F, Cl, Br, I, CN, aryl, heterocyclyl or a halogenated or unsubstituted alkyl radical having 1 to 15 carbon atoms, where, in addition, one or more CH₂ groups in this radical may each be replaced, independently of one another, by -C≡C-, -CH=CH-, -O-, -CO-, -CO-O- or -O-CO- in such a way that O atoms are not linked directly to one another;

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A stands for , or

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a is 0, 1 or 2;

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Z¹¹ represents a single bond, $-CH_2-CH_2-$, $-CF_2-CF_2-$, $-CF_2-CH_2-$, $-CH_2-CF_2-$, $-CH_2-O-$, $-O-CH_2-$, $-CF_2-O-$ or $-O-CF_2-$;

W denotes >CH- or >C=;

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independently of one another, stand for B and D,

$$- \sum_{\text{or } L^3}^{L^1}$$

independently of one another, are 0 or 1; b and d,

10 denotes =O, =C(SR¹²)(SR¹³), =CF₂, -H, -F, -CI, -Br, -I, -CN, Y^{11} -OH, -SH, -CO-R¹⁴, -OSO₂R¹⁵, -C(=S⁺R¹²)(-SR¹³)X,

one another;

 $-B(OR^{16})(OR^{17})$, $-BF_3Cat^+$, $-Si(OR^{18})(OR^{19})(OR^{20})$ or alkyl, where alkyl denotes a halogenated or unsubstituted alkyl radical having 1 to 15 C atoms, in which, in addition, one or more CH2 groups may each be replaced, independently of one another, by -C=C-, -CH=CH-, -O-, -CO-, -CO-O- or -O-CO- in such a way that O atoms are not linked directly to

Y¹² and Y¹³, independently of one another, denote H or alkyl, where alkyl denotes a halogenated or unsubstituted alkyl radical having 1 to 15 C atoms, in which, in addition, one or more CH₂ groups may each be replaced, independently of one another, by -C≡C-, -CH=CH-, -O-, -CO-, -CO-O- or -O-CO- in such a way that O atoms are not linked directly to one another;

L¹, L² and L³, independently of one another, denote H or F;

R¹² and R¹³, independently of one another, denote an unbranched or branched alkyl radical having 1 to 15 carbon atoms or toge R^{15}

ther form a $-(CH_2)_{p^-}$ unit, where p = 2, 3, 4, 5 or 6, where one, two or three of these CH_2 groups may be substituted by at least one unbranched or branched alkyl radical having 1 to 8 carbon atoms;

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R¹⁴ denotes OH, O-aryl, O-aralkyl, O-alkyl, Cl, Br, aryl, aralkyl or alkyl;

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denotes aryl, aralkyl or a halogenated or unsubstituted alkyl radical having 1 to 15 carbon atoms, where, in addition, one or more CH₂ groups in this alkyl radical may each be replaced, independently of one another, by -C≡C-, -CH=CH-, -O-, -CO-, -CO-O- or -O-CO- in such a way that O atoms are not linked directly to one another;

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 R^{16} and R^{17} denote H or an unbranched or branched alkyl radical having 1 to 15 carbon atoms or together form a -(CH₂)_p- unit, where p = 2, 3, 4, 5 or 6, where one, two or three of these CH₂ groups may be substituted by at least one unbranched or branched alkyl radical having 1 to 8 carbon atoms;

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R¹⁸, R¹⁹ and R²⁰, independently of one another, denote an unbranched or branched alkyl radical having 1 to 15 carbon atoms;

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Cat⁺ is an alkali metal cation or a quaternary ammonium cation;

and

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X is a weakly coordinating anion;

with the proviso

that W denotes >CH- if b+d \neq 0;

that Y¹¹ does not denote =O, =C(SR¹²)(SR¹³) or =CF₂ if Y¹¹ is con-

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nected to B or D =

that Y¹¹ denotes -H, -I, -OH, -SH, -CO₂R¹⁴, -OSO₂R¹⁵, $-C(=S^{+}R^{12})(SR^{13})X^{-}$, $-B(OR^{16})(OR^{17})$, $-BF_{3}Cat^{+}$, $-Si(OR^{18})(OR^{19})(OR^{20})$ or alkyl, where alkyl denotes a halogenated or unsubstituted alkyl radical having 1 to 15 C atoms, in which one or more CH₂ groups have each been replaced, independently of one another, by -C≡C-, -CH=CH-, -O-, -CO-, -CO-O- or -O-CO- in such a way that O atoms are not linked directly to one another and alkyl does not stand for

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$$\begin{array}{c|c} & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\ & &$$

alkoxy, if W is connected directly to where d is 0 or 1;

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that B does not stand for

that A can adopt identical or different meanings if a is 2.

2. 25

Compound according to Claim 1, characterised in that

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- 3. Compound according to Claim 1, characterised in that
- 30 is 0. а

 Compound according to any one of Claims 1 to 3, characterised in that
 Y¹² and Y¹³ denote H.

- 5 Compound according to any one of Claims 1 to 4, characterised in that
 Z¹¹ represents a single bond, -CF₂O- or -OCF₂-.
- 6. Compound according to any one of Claims 1 to 5, characterised in that

 R¹¹ denotes an unbranched halogenated or unsubstituted alkyl radical having 1 to 7 carbon atoms.
- 7. Compound according to any one of Claims 1 to 6, characterised in that $Y^{11} \qquad \text{denotes = O, =C(SR^{12})(SR^{13}) or =CF_2}.$
 - 8. Compound according to any one of Claims 1 to 6, characterised in that

 Y¹¹ denotes -H, -F, -Cl, -Br, -I, -OH, -CO₂H, -C(=S⁺R¹²)(-SR¹³)X

20 Y^{11} denotes -H, -F, -CI, -Br, -I, -OH, -CO₂H, -C(=S⁺R¹²)(-SR¹³)X⁻, -B(OR¹⁶)(OR¹⁷), -BF₃Cat⁺ or -Si(OR¹⁸)(OR¹⁹)(OR²⁰).

- 9. Compound according to any one of Claims 1 to 6 and 8, characterised in that
- 25 X denotes BF_4 , CF_3SO_3 , $C_4F_9SO_3$, PF_6 , SbF_6 or AsF_6 .
 - 10. Compound according to any one of Claims 1 to 9, characterised in thatb is 0 and d is 0.

11. Compound according to any one of Claims 1 to 9, characterised in that

b is 1 and d is 0.

- 12. Compound according to any one of Claims 1 to 9, characterised in that
- 5 b is 1 and d is 1.

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13. Process for the preparation of a compound of the formula IA

$$R^{11} - A_a - Z^{11} - O_{W-Y^{11}}$$
IA

in which

R¹¹ denotes H, F, Cl, Br, I, CN, aryl, heterocyclyl or alkyl;

A stands for , or

- a is 0, 1 or 2, where A can adopt identical or different meanings if a is 2;
 - Z¹¹ represents a single bond, $-CH_2-CH_2-$, $-CF_2-CF_2-$, $-CF_2-CH_2-$, $-CH_2-CF_2-$, $-CH_2-O-$, $-O-CH_2-$, $-CF_2-O-$ or $-O-CF_2-$;

W denotes >C=;

25 Y^{11} denotes =0, =C(SR¹²)(SR¹³) or =CF₂;

 Y^{12} and Y^{13} , independently of one another, denote H or alkyl; and R^{12} and R^{13} , independently of one another, denote an unbranched or branched alkyl radical having 1 to 15 carbon atoms or together form a -(CH_2)_p- unit, where p = 2, 3, 4, 5 or 6, where one, two or three of these CH_2 groups may be substituted by at least one unbranched or branched alkyl radical having 1 to 8 carbon atoms;

characterised in that a compound of the formula II

$$R^{11}$$
 A_a Z^{11} II

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in which R^{11} , A, a and Z^{11} are as defined above for the formula IA, is reacted in a reaction step (A1)

(A1) in the presence of a base with a compound of the formula III

in which Y¹² and Y¹³ are as defined above for the formula IA, and R³¹ denotes an alkyl radical having 1 to 15 carbon atoms, to give a compound of the formula IV

$$R^{11}$$
 A_a Z^{11} $COOR^{31}$ V

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in which R^{11} , A, a, Z^{11} , Y^{12} and Y^{13} are as defined above for the formula IA, and R^{31} is as defined above for the formula III; and subsequently, in a reaction step (A2),

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(A2) the compound of the formula IV is converted into the compound IA1

$$R^{11} - A_a - Z^{11}$$
 O IA1

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and optionally, in a reaction step (A3),

- 43 -

(A3) the compound of the formula IA1 is converted into the compound IA2

$$R^{11}$$
 A_a Z^{11} CF_2 IA2

by reaction with CF_2Br_2 in the presence of $P(N(R^{21})_2)_3$, $P(N(R^{21})_2)_2(OR^{22})$ or $P(N(R^{21})_2)(OR^{22})_2$, where R^{21} and R^{22} , independently of one another, denote an alkyl radical having 1 to 15 carbon atoms;

or optionally, in a reaction step (A3'),

(A3') the compound of the formula IA1 is converted into the compound IA3

$$R^{11}$$
 A_a Z_{12}^{11} A_a A_a

by reaction with CHG(SR¹²)(SR¹³), in which G denotes P(OCH₂R²³)₃, where R²³ is a perfluorinated alkyl radical having 1 to 5 carbon atoms, or Si(CH₃)₃ or Si(CH₂CH₃)₃, and R¹² and R¹³ are as defined above for the formula IA, in the presence of a strong base.

14. Process for the preparation of a compound of the formula IB

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$$R^{11} - A_a - Z^{11}$$
 $Y^{12} - Y^{13} + Z^{11}$ $Y^{13} + Z^{11} +$

in which

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30 R¹¹ denotes H, F, Cl, Br, I, CN, aryl, heterocyclyl or alkyl;

- 44 -

A stands for o

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a is 0, 1 or 2, where A can adopt identical or different meanings if a is 2;

Z¹¹ represents a single bond, $-CH_2-CH_2-$, $-CF_2-CF_2-$, $-CF_2-CH_2-$, $-CH_2-CF_2-$, $-CH_2-O-$, $-O-CH_2-$, $-CF_2-O-$ or $-O-CF_2-$;

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Y¹¹ denotes -H, -F, -Cl, -Br, -I, -CN, -OH or -B(OR¹⁶)(OR¹⁷);

Y¹² and Y¹³, independently of one another, denote H or alkyl; L¹, L² and L³, independently of one another, denote H or F; and R¹⁶ and R¹⁷, independently of one another, denote H or an un-

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branched or branched alkyl radical having 1 to 15 carbon atoms or together form a $-(CH_2)_{p^-}$ unit, where p = 2, 3, 4, 5 or 6, where one, two or three of these CH_2 groups may be substituted by at least one unbranched or branched alkyl radical having 1 to 8 carbon atoms;

characterised in that,

in a reaction step (B1),

(B1) a compound of the formula IA1

$$R^{11} - A_a - Z^{11} - O$$
 $Y^{12} - Y^{13}$
IA1

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in which R¹¹, A, a, Z¹¹, Y¹² and Y¹³ are as defined above for the formula IB,

is reacted with a compound of the formula V

$$M \longrightarrow Q$$
 V

in which L¹, L² and L³ are as defined above for the formula IB, M denotes Li, Cl-Mg, Br-Mg or I-Mg, and Q denotes H, F, Cl, Br, I or CN, with formation of the compound of the formula IB1

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$$R^{11}$$
 A_a $Z_{Y^{12}}^{11}$ A_a A

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in which R¹¹, A, a, Z¹¹, Y¹², Y¹³, L¹, L² and L³ are as defined for the formula IB, and Q is as defined for the formula V; and optionally, in a reaction step (B2),

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(B2) the compound of the formula IB1 in which Q denotes Br is reacted with $B(OR^{16})(OR^{17})(OR^{24})$, where R^{16} , R^{17} and R^{24} are an unbranched or branched alkyl radical having 1 to 15 carbon atoms, or with $HB(OR^{16})(OR^{17})$, where R^{16} and R^{17} denote an unbranched or branched alkyl radical having 1 to 15 carbon atoms or together form a $-(CH_2)_p$ - unit, where p=2, 3, 4, 5 or 6, where one, two or three of these CH_2 groups may be substituted by at least one unbranched or branched alkyl radical having 1 to 8 carbon atoms, in the presence of an alkyllithium base,

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to give the compound of the formula IB2

$$R^{11}$$
 A_a Z^{11} A_a A_a

and optionally, in a reaction step (B3),

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(B3) the compound IB2 is converted into the compound IB3

$$R^{11}$$
 A_a Z_{12}^{11} A_a A_a

by reaction with an aqueous acid;

and/or optionally, in a reaction step (B4),

(B4) the compound IB2 or the compound IB3 is converted into the compound IB4

$$R^{11}$$
 A_a Z^{11} Y^{12} Y^{13} Z^{3} Z^{2} OH IB4

by reaction with hydrogen peroxide in alkaline or acidic solution.

15. Process for the preparation of a compound of the general formula IC

$$R^{11} - A_a - Z^{11}$$
 Y^{12} Y^{13} Y^{11}

in which

R¹¹ denotes H, F, Cl, Br, I, CN, aryl, heterocyclyl or alkyl;

a is 0, 1 or 2, where A can adopt identical or different meanings if a is 2;

Z¹¹ represents a single bond, $-CH_2-CH_2-$, $-CF_2-CF_2-$, $-CF_2-CH_2-$, $-CH_2-CF_2-$, $-CH_2-O-$, $-O-CH_2-$, $-CF_2-O-$ or $-O-CF_2-$;

10 Y¹¹ denotes

denotes =0, = $C(SR^{12})(SR^{13})$ or = CF_2 ;

 Y^{12} and Y^{13} , independently of one another, denote H or alkyl; and R^{12} and R^{13} , independently of one another, denote an unbranched or branched alkyl radical having 1 to 15 carbon atoms or together form a -(CH₂)_p- unit, where p = 2, 3, 4, 5 or 6, where one, two or three of these CH₂ groups may be substituted by at least one unbranched or branched alkyl radical having 1 to 8 carbon atoms;

characterised in that, in a reaction step (C1),

(C1) the compound of the formula IB4

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$$R^{11}$$
 A_a Z_{12}^{11} A_a A_a

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in which R^{11} , A, a, Z^{11} , Y^{12} and Y^{13} are as defined above for the formula IC, and L^1 , L^2 and L^3 denote H, is converted into the compound IC1

$$R^{11} - A_a - Z^{11}$$
 O IC1

using hydrogen in the presence of a transition-metal catalyst; and optionally, in a reaction step (C2),

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(C2) the compound IC1 is converted into the compound IC2

$$R^{11} - A_a - Z^{11}$$
 CF_2 CF_2

by reaction with CF_2Br_2 in the presence of $P(N(R^{21})_2)_3$, $P(N(R^{21})_2)_2(OR^{22})$ or $P(N(R^{21})_2)(OR^{22})_2$, where R^{21} and R^{22} , independently of one another, are an alkyl radical having 1 to 15 carbon atoms; or optionally, in a reaction step (C2'),

(C2') the compound of the formula IC1 is converted into the compound IC3

$$R^{11}$$
 A_a Z_{12}^{11} A_a A_a

by reaction with CHG(SR¹²)(SR¹³), in which G denotes P(OCH₂R²³)₃, where R²³ is a perfluorinated alkyl radical having 1 to 5 carbon atoms, or Si(CH₃)₃ or Si(CH₂CH₃)₃, and R¹² and R¹³ are as defined above for the formula IC, in the presence of a strong base.

16. Process for the preparation of a compound of the formula ID

$$R^{11} - A_a - Z_{12}^{11} - O_{13} + C_{13}^{13} + C_{13}^{11}$$
 ID

in which

 R^{11} denotes H, F, Cl, Br, I, CN, aryl, heterocyclyl or alkyl;

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is 0, 1 or 2, where A can adopt identical or different meanings а if a is 2;

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 Z^{11} represents a single bond, -CH₂-CH₂-, -CF₂-CF₂-, -CF₂-CH₂-, -CH₂-CF₂-, -CH₂-O-, -O-CH₂-, -CF₂-O- or -O-CF₂-;

 Y^{11}

denotes $-CO_2H$ or $-C(=S^+R^{12})(-SR^{13})X^-$;

Y¹² and Y¹³, independently of one another, denote H or alkyl;

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L¹, L² and L³, independently of one another, denote H or F;

R¹² and R¹³, independently of one another, denote an unbranched or branched alkyl radical having 1 to 15 carbon atoms or together form a - $(CH_2)_{p}$ - unit, where p = 2, 3, 4, 5 or 6, where one, two or three of these CH2 groups may be substituted by at least one unbranched or branched alkyl radical having 1 to 8 carbon atoms; and

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χĪ is a weakly coordinating anion; characterised in that, in a reaction step (D1),

(D1) a compound of the formula IB1

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$$R^{11} - A_a - Z^{11}$$
 Q Q IB1

in which R¹¹, A, a, Z¹¹, Y¹², Y¹³, L¹, L² and L³ are as defined for the formula ID, and Q denotes H or Br,

is reacted with an organometallic base and CO₂ to give the compound ID1

$$R^{11} - A_a - Z^{11}$$
 CO_2H ID1

in which R¹¹, A, a, Z¹¹, Y¹², Y¹³, L¹, L² and L³ are as defined for the formula ID;

and optionally, in a reaction step (D2),

(D2) the compound ID1 is converted into the compound ID2

$$R^{11}$$
 A_a Z_a^{11} A_a $A_$

in the presence of an acid HX using HSR¹² and HSR¹³ or using HSR¹²R¹³SH.

17. Process for the preparation of a compound of the formula IE

$$R^{11} - A_a - Z_{11}^{11} - Q_{13}^{13}$$

in which

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R¹¹ denotes H, F, Cl, Br, I, CN, aryl, heterocyclyl or alkyl;

A stands for ,
$$\longrightarrow$$
 , \longrightarrow or

a is 0, 1 or 2, where A can adopt identical or different meanings if a is 2;

Z¹¹ represents a single bond, $-CH_2-CH_2-$, $-CF_2-CF_2-$, $-CF_2-CH_2-$, $-CH_2-CF_2-$, $-CH_2-O-$, $-O-CH_2-$, $-CF_2-O-$ or $-O-CF_2-$;

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 Y^{11} denotes -CO₂H or -C(=S⁺R¹²)(-SR¹³)X⁻;

Y¹² and Y¹³, independently of one another, denote H or alkyl;

 R^{12} and R^{13} , independently of one another, denote an unbranched or branched alkyl radical having 1 to 15 carbon atoms or together form a -(CH₂)_p- unit, where p = 2, 3, 4, 5 or 6, where one, two or three of these CH₂ groups may be substituted by at least one unbranched or branched alkyl radical having 1 to 8 carbon atoms; and

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X is a weakly coordinating anion; characterised in that, in a reaction step (E1),

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(E1) the compound of the formula ID1

$$R^{11}$$
 A_a Z^{11} A_a CO_2H ID1

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in which R^{11} , A, a, Z^{11} , Y^{12} and Y^{13} are as defined above for the formula IE, and L^1 , L^2 and L^3 denote H, is converted into the compound IE1

$$R^{11}$$
 A_a Z_{12}^{11} CO_2H IE1

using hydrogen in the presence of a transition-metal catalyst; and optionally, in a reaction step (E2),

(E2) the compound of the formula IE1 is converted into the compound IE2

$$R^{11}$$
 A_a Z_{12}^{11} A_a Z_{13}^{12} A_a A_a

in the presence of an acid HX using HSR¹² and HSR¹³ or using HSR¹²R¹³SH.

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